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(71) Applicants: TOKAI  
DENKA KOGYO  
KABUSHIKI KAISHA,  
ROOM 428  
OHTEMACHI  
BUILDING, 6-1, 1-  
CHOME,  
OHTEMACHI,  
CHIYODA-KU,  
TOKYO, JAPAN

(72) Inventor:  
KATSUTOSHI ITANI

(74) Agents: D. YOUNG &  
CO.,

(54) CONTROLLING STAINLESS  
STEEL PICKLING SOLUTION BY  
HYDROGEN PEROXIDE AND  
SULPHURIC ACID ADDITION.

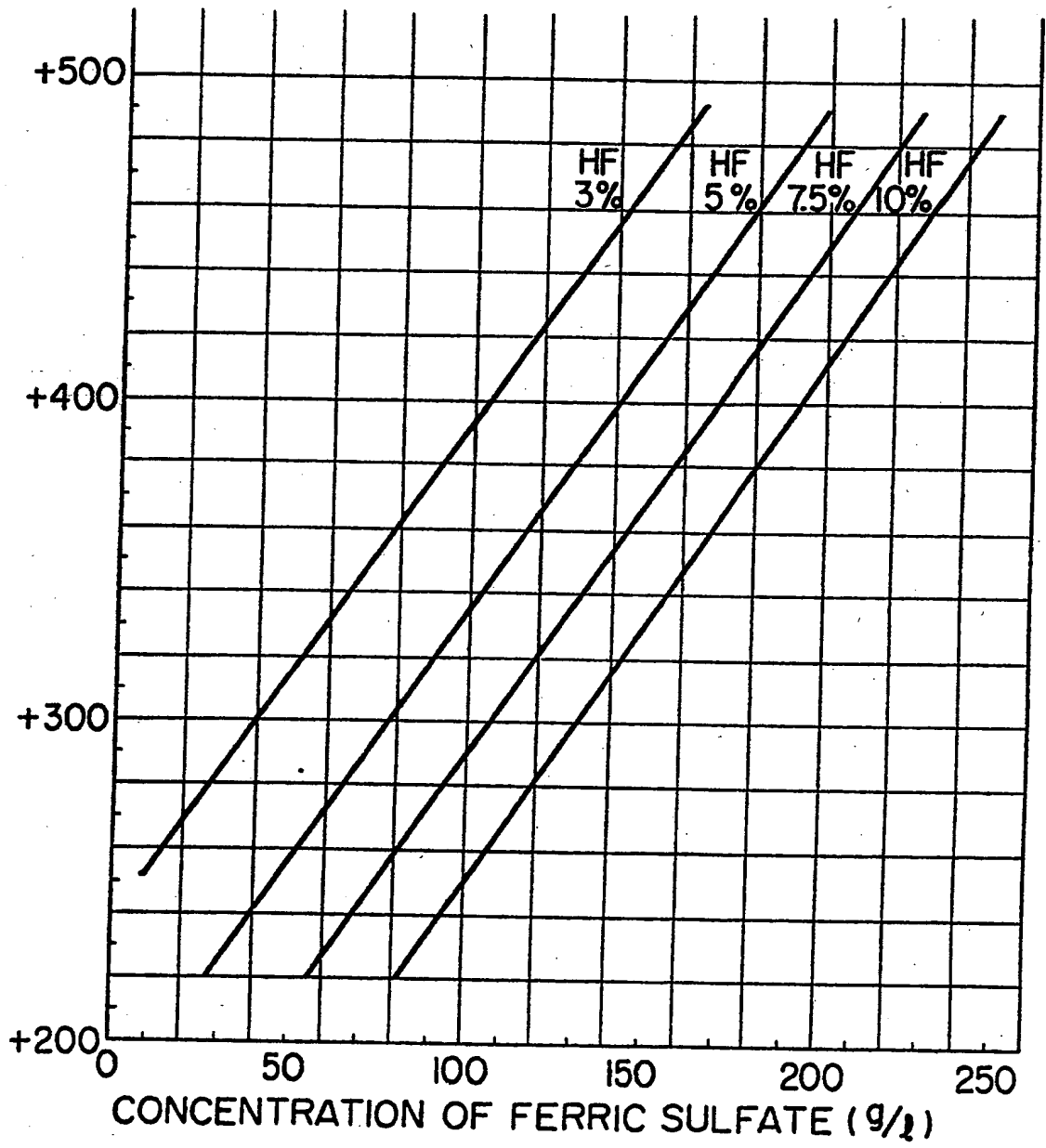
(57) According to the present  
invention, there is provided a method  
for controlling the composition of a

pickling solution characterized in that  
in the pickling for stainless steel using  
a ferric sulfate-hydrofluoric acid bath,  
the oxidation-reduction potential of  
the pickling solution is held in a  
predetermined range by adding  
hydrogen peroxide and sulfuric acid  
into the pickling solution.

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## SPECIFICATION

## METHOD FOR CONTROLLING PICKLING SOLUTION OF STAINLESS STEEL

This invention relates to a method for controlling the composition of a pickling solution of stainless steel.

More particularly, in the pickling for stainless steel using a ferric sulfate-hydrofluoric acid bath, this invention is concerned with a method of controlling the composition of the pickling solution through adjustment of the oxidation-reduction potential of the same solution.

In the conventional descaling pickling method for stainless steel, two to four inorganic acids are selected from such inorganic acids as sulfuric acid, hydrochloric acid, nitric acid, hydrofluoric acid and phosphoric acid according to the kind of the material to be pickled, the degree of adhesion of annealing scale, and the purpose of pickling.

Above all, a pickling solution consisting of a mixed nitric-hydrofluoric acid is generally used widely. This pickling solution has a sufficient pickling ability, but its repeated use tends to lower the pickling ability comparatively in an early stage. To prevent this, it is required to replenish nitric acid and hydrofluoric acid intermediate in pickling, or to newly make the same bath. Thus, it is very troublesome to control the pickling solution.

In the case of such conventional pickling solution, moreover, an environmental pollution due to the generation of NO<sub>x</sub> (nitrogen oxide gases) gas now causes a serious social problem. Various methods of treating NO<sub>x</sub> gas have been proposed, but at present there is no method that is technically free of drawback and economical. Therefore, such a pickling solution as does not generate NO<sub>x</sub> gas is requested and many proposals have been made, among which a pickling method using a ferric sulfate-hydrofluoric acid bath is known.

However, such pickling solution ages in a short period, so that many operations are needed, for example, replenishing chemicals or making a new bath. It is more troublesome in the control of pickling solution and less economical than the mixed nitric-hydrofluoric acid bath which is now generally used widely. Therefore, such conventional pickling solution is not practical.

Moreover, as the method of preparing a ferric sulfate solution, it is publicly known to obtain ferric sulfate by oxidizing a ferrous sulfate solution with hydrogen peroxide and sulfuric acid. From this, it is inevitably conceivable and publicly known that in a ferric sulfate-hydrofluoric acid bath, the ferrous sulfate which is primarily produced in the pickling solution for stainless steel when pickled is oxidized using hydrogen peroxide and sulfuric acid to regenerate ferric sulfate, and the latter is used repeatedly in the pickling. Even in this method, however, it is very difficult to control the concentration of ferric sulfate when aged after pickling and the concentration thereof after regeneration by the oxidation with hydrogen peroxide and sulfuric acid. This difficulty causes a problem, and so this method is not actually adopted.

The foregoing problems associated with the conventional pickling methods, are solved according to the present invention characterized in that in the pickling of stainless steel using a ferric sulfate-hydrofluoric acid bath, the oxidation-reduction potential of the pickling solution is held in a predetermined range by adding hydrogen peroxide and sulfuric acid into the pickling solution. The addition of the hydrogen peroxide and sulfuric acid can be done continuously while pickling stainless steel.

An excellent feature of the present invention resides in that by only a simple operation of adding hydrogen peroxide and sulfuric acid so as to maintain the oxidation-reduction potential in a constant range, ferric sulfate can be held in a constant range of concentration without the need for a chemical analysis of the composition with the result that uniform surface finish and pickling time can be achieved.

Furthermore, according to the method of the present invention, it becomes possible to make a complete automation, continuation and solution closing, with NO<sub>x</sub> gas not generated and the amount of waste liquor to be treated largely decreased. Thus, the method of the present invention is an epoch-making method which has remedied the drawbacks encountered in the prior art pickling methods. Besides, as compared with the conventional ferric sulfate-hydrofluoric acid bath, the pickling cost can be reduced to a large extent; and even in comparison with the nitric acid-hydrofluoric acid bath presently in use, a low cost comparable thereto can be attained.

Figure 1 shows the results of measurement of the oxidation-reduction potential in the form of a graph which results serve as basic data for working the method of controlling a pickling solution of the present invention in which measurement the concentration of ferrous sulfate in the pickling solution was 30 grams per litre and the concentration of ferric sulfate and that of hydrofluoric acid (HF) were varied, and the oxidation-reduction potential of each was measured at the solution temperature of 50°C.

In working the present invention, the concentration range of ferric sulfate and that of hydrofluoric acid are predetermined according to the kind of material to be pickled, the degree of annealing scale and the purpose of pickling, and further the range of oxidation-reduction potential in balance therewith is decided. And hydrogen peroxide and sulfuric acid are added and pickling is carried out within such range of oxidation-reduction potential.

It is desired that the molar ratio of hydrogen peroxide and sulfuric acid to be added be about 1:1.

The concentration of hydrogen peroxide and that of sulfuric acid to be used are not specially restricted.

If the pickling for stainless steel is carried out in a ferric sulfate-hydrofluoric acid bath, the ferric sulfate is consumed for the dissolving of stainless steel and there are produced ferrous sulfate, chromium sulfate and nickel sulfate according to the composition of the material to be pickled. On the other hand, the hydrofluoric acid is partially consumed as hydrogen ion in the dissolving of stainless steel, but fluoride ion is not consumed and exists in the pickling solution. The consumed hydrogen ion can be replenished by slightly increasing the amount of sulfuric acid to be added in the oxidation-regeneration operation. If pickling is continued, there accumulate in the solution ferrous sulfate in an amount exceeding the necessary amount for the regeneration of ferric sulfate, and also unoxidized chromium sulfate and nickel sulfate.

It is mainly the concentration of ferric sulfate and that of hydrofluoric acid that affect the oxidation-reduction potential of the pickling solution. Ferrous sulfate somewhat affects the same potential. Chromium sulfate and nickel sulfate have no influence. It has become clear that in case a measurement of oxidation-reduction potential is made by changing the concentration of ferric sulfate and that of hydrofluoric acid, there is nearly a straight-line relationship between the concentration of ferric sulfate and the oxidation-reduction potential, and that the straight line shifts in a parallel manner by the change in hydrofluoric acid concentration. As previously noted, fluoride ion in the solution is not consumed and exists, so that if the concentration of hydrofluoric acid in the pickling solution is maintained constant, the oxidation-reduction potential becomes corresponding to the change in ferric sulfate concentration. The concentration of ferrous sulfate affects the oxidation-reduction potential in such a manner that in case the concentration of ferric sulfate and that of hydrofluoric acid are made constant, the oxidation-reduction potential tends to decrease as the concentration of ferrous sulfate becomes higher. In this case, however, the decreasing degree of the oxidation-reduction potential is not so large.

Therefore, with these facts taken into account in advance, it is necessary to be aware of the minimum concentration of ferric sulfate required for pickling, regard the oxidation-reduction potential at that time as the minimum potential and maintain the potential always above the minimum value during pickling and regeneration, whereby even if the oxidation-reduction potential somewhat decreases due to the presence of ferrous sulfate which gradually accumulates in the solution, it has no influence upon process control, and uniform pickling finish and pickling time can be achieved. It has become clear that the change in concentration of ferrous sulfate due to its accumulation does not greatly affect the oxidation-reduction potential up to its concentration of about 200 g/l. At a concentration of ferrous sulfate above 200 g/l, it is deposited as crystals (mainly  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) on standing at room temperature. Therefore, through combination with this method it is also possible to keep the concentration of ferrous sulfate below 200 g/l. The amount of ferrous-, chromium- and nickel-sulfate which accumulate in the pickling solution differs according to the amount of solution brought out of the system in an adhered state of steel after pickling. The larger the amount of solution brought out of the system, the smaller becomes the amount of sulfates which accumulate. At the same time, however, fluoride ion is also brought out of the system, so it is necessary to replenish hydrofluoric acid on the basis of a calculated amount, or alternatively measure the concentration of fluoride ion using an ion meter or the like and replenish hydrofluoric acid.

Conversely, in case the amount of solution brought out of the system is small and the amount of sulfates which accumulate becomes large, the amount of solution to be drawn out is determined so as to give a concentration not affecting the oxidation-reduction potential. In this case, there is adopted a method in which the solution is drawn out continuously or intermittently, or a method in which the bath is cooled for removal as crystals outside the system.

These operations can be made regular once pickling is experienced. The oxidation-reduction potential of the pickling solution is affected by temperature, so when measuring such potential it is necessary to pay attention so that the temperature is the same.

With respect to the electrodes used in the measurement of the oxidation-reduction potential, as a reference electrode there may be used those which are normally in use, for example, a saturated calomel electrode and a silver chloride electrode, and as a measuring electrode there may be used any electrodes if only they are inert to the pickling solution, for example, noble metal electrodes such as platinum, gold and rhodium.

The following examples are given to further illustrate the present invention:

#### EXAMPLE 1.

With the concentration of ferrous sulfate of 30 g/l, the concentration of ferric sulfate and that of hydrofluoric acid were varied and the oxidation-reduction potential of each was measured at the solution temperature of 50°C, the results of which are shown in Figure 1 hereto attached.

In the above measurement of the oxidation-reduction potential, a saturated calomel electrode was used as a reference electrode and a platinum electrode as a measuring electrode.

#### EXAMPLE 2.

Into pickling solutions containing ferric sulfate and hydrofluoric acid in amounts set out in Table 1 below were added ferrous sulfate in concentrations of 30 g/l, 100 g/l and 200 g/l and chromium- and

nickel-sulfate in concentrations of 20 g/l and 40 g/l as chromium plus nickel (whose ration was 1:1). Using the same electrodes as in Example 1, the oxidation-reduction potential of each pickling solution at 50°C was measured, the results of which are shown in Table 1.

### EXAMPLE 3.

5 A pickling solution containing 150 g/l of ferric sulfate, 5% of hydrofluoric acid and 30 g/l of ferrous sulfate was prepared. With the pickling solution thus prepared, annealing scales respectively of pipe, bar wire and plane sheets of SUS 304, 308 and 316 were pickled continuously. Using the same electrodes as in Example 1 and with the pickling temperature held at 50°C, the minimum value of the oxidation-reduction potential was set to +300mV and hydrogen peroxide (35%) and sulfuric acid (98%) were added at times in the molar ratio of 1:1 so that the oxidation-reduction potential was kept above +300mV at all times during pickling. The amount of the pickling solution was adjusted according to the amount of hydrogen peroxide and sulfuric acid used for the oxidation-regeneration and the amount of solution brought out of the system in an adhered state to the samples after descaling. And a small amount of hydrofluoric acid was replenished at times.

15 As the pickling proceeded in a continuous manner, ferrous-, chromium- and nickel-sulfate accumulated gradually and reached the respective concentrations of 180 g/l, 14 g/l as chromium and 16 g/l as nickel. Even at this moment, a constant pickling time just the same as that in the initial bath and a good finish were achieved.

TABLE 1

Experiment No.	1	2	3	4
Concentration of ferric sulfate	150 g/l	150 g/l	150 g/l	150 g/l
Concentration of ferrous sulfate	30 g/l	100 g/l	200 g/l	30 g/l
Concentration of chromium + nickel	—	—	—	20 g/l
Concentration of hydrofluoric acid	5%	5%	5%	5%
Oxidation-reduction potential	+415mV	+395mV	+370mV	+410mV

Experiment No.	5	6	7	8
Concentration of ferric sulfate	150 g/l	150 g/l	100 g/l	100 g/l
Concentration of ferrous sulfate	30 g/l	200 g/l	30 g/l	200 g/l
Concentration of chromium + nickel	40 g/l	40 g/l	—	—
Concentration of hydrofluoric acid	5%	5%	5%	5%
Oxidation-reduction potential	+410mV	+370mV	+335mV	+295mV

### 20 CLAIMS

1. Method for controlling the composition of pickling solution characterized in that in the pickling for stainless steel using a ferric sulfate-hydrofluoric acid bath, the oxidation-reduction potential of the pickling solution is held in a predetermined range by adding hydrogen peroxide and sulfuric acid into the pickling solution.

25 2. Method according to Claim 1, characterized in that hydrogen peroxide and sulfuric acid are added in the molar ratio of 1:1.

3. Method according to Claim 1, characterized in that the ferrous sulfate in the pickling solution is maintained in a concentration below 200 g/l.

30 4. Method according to Claim 1, characterized in that each measurement of the oxidation-reduction potential is made with respect to the pickling solution at the same temperature.

